

Determination of Oxirane Oxygen

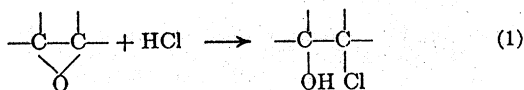
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A general procedure for the determination of oxirane oxygen is described. The method, originally proposed by Nicolet and Poulter, is based upon the quantitative opening of the oxirane ring by means of a 0.2 *N* solution of anhydrous hydrogen chloride in absolute ethyl ether. The method is specific for the determination of oxirane oxygen, it may be employed

in the analysis and determination of the purity of a wide variety of oxirane compounds, and it is suitable for the determination of oxirane oxygen in air-oxidation reaction mixtures. The reaction of anhydrous hydrogen chloride with oxirane compounds in absolute ethyl ether solution is suggested as a general method for preparing chlorohydrins.

IN STUDYING the mechanism of the air oxidation of unsaturated fatty materials, it is essential to determine the quantity of each of several types of oxygen-containing groups in the product. It is customary to analyze for hydroxyl, carboxyl, carbonyl, and ester oxygen, but no work has been reported on the determination of oxirane oxygen ($\begin{array}{c} \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$) in such materials, even

though it is well known that oxirane compounds are formed during the air or oxygen oxidation of unsaturated compounds (3, 4). Recently, Hilton (6) has suggested a method for determining oxirane oxygen in oxidized rubber, the basis for which is the reaction of diethylamine with the oxirane group under pressure in a sealed tube, followed by analysis of the reaction product for nitrogen. This method is time-consuming and inconvenient, and it is not suitable for control work. The method of Nicolet and Poulter (7), however, appears to be admirably suited for the analysis of air-oxidation reaction mixtures for oxirane oxygen. This method which is based upon the quantitative opening of the oxirane ring by means of a solution of anhydrous hydrogen chloride in absolute ethyl ether (Equation 1):



was applied by them only to the analysis of the 9,10-epoxystearic acids, derivable for oleic and elaidic acids. But whether the method is specific for oxirane oxygen and whether it is applicable to a variety of oxirane compounds in which the oxirane group is at different positions in the molecule had to be determined before it could be employed for the analysis of air-oxidation mixtures.

REAGENTS

All chemicals should be A.C.S. analytical reagent grade. **Anhydrous Hydrogen Chloride, 0.2 *N*, in Absolute Ethyl Ether.** Pass anhydrous hydrogen chloride gas into 1500 ml. of absolute ethyl ether until a blank titration indicates that the solution is 0.19 to 0.2 *N*. Conduct this titration by pipetting 25 ml. of the solution into 50 ml. of 95% ethyl alcohol and titrating with 0.1 *N* sodium hydroxide solution. Prepare anhydrous hydrogen chloride by the dropwise addition of concentrated hydrochloric acid to concentrated sulfuric acid (2). Approximately 25 to 35 ml. of concentrated hydrochloric acid is used, and the operation takes 30 minutes to 1 hour.

Indicator. Dissolve 1 gram of phenolphthalein in 100 ml. of 95% ethyl alcohol.

Sodium Hydroxide. Carefully standardized 0.1 *N* sodium hydroxide solution.

PROCEDURE

Weigh sample in accordance with the expected content of oxirane oxygen, as shown in Table I, into a 250-ml. Erlenmeyer flask with a hollow 24/40 $\frac{1}{2}$ ground-glass stopper. (Because of its light weight the hollow stopper acts as an automatic safety valve and makes unnecessary the manual release of pressure required to prevent breakage resulting from violent ejection of the

heavier solid stopper.) Liquids are weighed by difference from dropping bottles; solids are weighed into tared flasks. The maximum weight of sample should be taken only when it is known that the oxirane oxygen content lies near the minimum value of the range given. Adherence to these values will ensure a proper (at least 100%) excess of hydrochloric acid-ether solution. Wash down the sides of the flask with 5 ml. of absolute ethyl ether and add exactly 25 ml. of the hydrochloric acid-ether solution. Stopper the flask and swirl gently to dissolve the sample. Allow the solution to stand for 3 hours at room temperature. Add 50 ml. of 95% ethyl alcohol and 1 ml. of the phenolphthalein indicator solution, and titrate the excess acid with 0.1 *N* sodium hydroxide solution. Conduct at least two blank determinations, which must check within 0.1 ml.

In order to calculate the percentage of oxirane oxygen, the acid content of the sample, expressed as milliliters of sodium hydroxide, must be determined. Weigh a separate sample (0.3 to 2.0 grams) into a 250-ml. Erlenmeyer flask and dissolve in 75 ml. of freshly neutralized 95% ethyl alcohol, heating to dissolve if necessary. Oils insoluble in alcohol are refluxed with the alcohol for 5 minutes and then cooled to room temperature. If the solution has been heated, it must be cooled to room temperature. Titrate to a phenolphthalein end point with 0.1 *N* sodium hydroxide solution.

Table I. Recommended Sample Weights for Oxirane Oxygen Determination

Oxirane Oxygen Expected %	Weight of Sample Gram
1 to 4	1.0 to 0.8
4 to 8	0.8 to 0.4
8 to 12	0.4 to 0.25
12 to 16	0.25 to 0.20
16 to 20	0.20 to 0.15

The percentage of oxirane oxygen is calculated as follows:

$$\% \text{ oxirane oxygen} = \frac{B - (T - A) \times \text{normality} \times 0.016}{W} \times 100$$

B = ml. of sodium hydroxide used in blank

T = ml. of sodium hydroxide used in back-titration

A = acid content of sample expressed as ml. of sodium hydroxide required to neutralize the acid in *W* grams of sample

W = weight of sample

RESULTS AND DISCUSSION

The results obtained when the procedure described above was applied to a variety of purified oxirane compounds are shown in Table II. The compounds were analyzed immediately after purification. In virtually every case good concordance with the theoretical values was obtained. The only oxirane compounds which did not give satisfactory results were 1-phenyl-1,2-epoxyethane (styrene oxide) and 9,10,12,13-diepoxyoctadecanoic acid. The low result obtained with styrene oxide may be explained on the assumption that the hydrochloric acid-ether reagent caused a portion of this compound to isomerize to an aldehyde or ketone.

Table II. Analyses of Purified Oxirane Compounds

Compounds Analyzed (5, 8, 9, 10)	Per Cent Oxirane Oxygen	
	Calcd.	Found
9,10-Epoxystearic acid, m.p. 59.5°	5.36	5.33
9,10-Epoxystearic acid, m.p. 55°	5.36	5.35
9,10-Epoxyoctadecanol, m.p. 54°	5.62	5.65
9,10-Epoxyoctadecanol, m.p. 48°	5.62	5.60
9,10,12,13-Diepoxystearic acid, m.p. 78°	10.2	9.16
9,10,12,13-Diepoxystearic acid, m.p. 16°	5.12	5.08
Methyl 9,10-epoxystearate, m.p. 16°	7.47	7.28
Methyl 10,11-epoxyhendecanoate	17.3	16.8
Epichlorohydrin (Eastman White Label, redistilled)	12.6	12.3
Glycidol	12.5	12.0
1,2-Epoxyoctane	10.2	10.0
1,2-Epoxydecane	8.68	8.53
1,2-Epoxydodecane	7.54	7.53
1,2-Epoxytetradecane	13.3	11.7
1-Phenyl-1,2-epoxyethane (styrene oxide)		

It is well known that such isomerization is catalyzed by acidic materials (11). That this assumption is probably valid and that this result is not due to incomplete reaction is shown by the fact that a 6-hour reaction time gives exactly the same result—namely, 11.7% oxirane oxygen. 9,10,12,13-Diepoxystearic acid was probably impure, since its melting point was 1° low (8), which would account for the low value.

Table III. Analyses of Mixtures of 9,10-Epoxystearic Acid (Melting Point 59.5°) and Benzoyl Peroxide for Oxirane Oxygen

Mixture	Per Cent Oxirane Oxygen	
	Calcd.	Found
Benzoyl peroxide, 100% ^a	0.0	0.0
9,10-Epoxystearic acid, 0%		
Benzoyl Peroxide, 23.1%	4.12	4.09
9,10-Epoxystearic acid, 76.9%		
Benzoyl peroxide, 20.5%	4.26	4.21
9,10-Epoxystearic acid, 79.5%		
Benzoyl peroxide, 12.5%	4.69	4.64
9,10-Epoxystearic acid, 87.5%		
Benzoyl peroxide, 8.3%	4.91	4.86
9,10-Epoxystearic acid, 91.7%		
Benzoyl peroxide, 4.4%	5.12	5.11
9,10-Epoxystearic acid, 95.6%		
Benzoyl peroxide, 0%	5.36	5.33
9,10-Epoxystearic acid, 100%		

^a Acidity determined in 100 ml. of ether-95% ethyl alcohol (1 to 3)

In order to determine whether the method is specific for oxirane oxygen the authors analyzed a variety of other compounds which do not contain this group but which contain functional groups usually encountered in air-oxidation reaction mixtures. The following compounds showed an oxirane oxygen content of less than 0.05%: 9,10-dihydroxystearic acids, chlorohydroxystearic acids, 10-ketostearic acid [also studied by Nicolet and Poulter (7)], oleic acid, oleyl alcohol, dioxane, tetrahydrofurfuryl alcohol, furfuryl alcohol, *n*-butyraldehyde, benzaldehyde, eleostearic acid, benzoyl peroxide, and *tert*-butyl hydroperoxide (50% solution in *tert*-butyl alcohol). The fact that these compounds do not react with the hydrochloric acid-ether reagent indicates that the isolated double bond, the primary alcohol group, the secondary alcohol group, the α -glycol group, the carbonyl group, the carboxyl group, conjugated double bonds, the organic peroxide and hydroperoxide groups, and epoxy groups other than oxirane, do not interfere with the use of the reagent. Since methyl 9,10-epoxystearate and methyl 10,11-epoxyhendecanoate give correct oxirane oxygen analyses (Table II), it can also be concluded that the ester group does not interfere. In addition, the authors have analyzed mixtures of 9,10-epoxystearic acid, melting point 59.5°, with benzoyl peroxide, and also with *tert*-butyl hydroperoxide in order to determine whether peroxides reduce the accuracy of the method. The results are shown in Tables III and IV.

From the data in Tables III and IV, it is evident that benzoyl peroxide and *tert*-butyl hydroperoxide do not reduce the accuracy of the method. The fact that oxirane oxygen can be determined

with great accuracy in the presence of large proportions of peroxides is of considerable importance in studying air-oxidation reactions. Crotonaldehyde and mesityl oxide, however, react with the hydrochloric acid-ether reagent to a limited extent, and oxirane oxygen analyses obtained on air-oxidation mixtures may be slightly in error if much α,β -unsaturated carbonyl compounds are present. It is unlikely that compounds with such structures would accumulate in actively oxidizing systems and the authors believe that such errors can be ignored.

Although Nicolet and Poulter (7) recommended that 0.1 to 0.2 *N* solutions of anhydrous hydrogen chloride in absolute ether be used, the authors have found that more reproducible results are obtained with 0.2 *N* solution. In the majority of instances, a 2-hour reaction period, as proposed by Nicolet and Poulter, is adequate, but in the case of certain oxirane compounds, notably 9,10-epoxystearic acid, melting point 55° (prepared from elaidic acid), a 3-hour reaction period gives closer checks between duplicate analyses, and values closer to the theoretical. For these reasons, the authors have standardized on the use of 0.2 *N* solution and a 3-hour reaction period. The longer reaction period and the more concentrated solution are especially important when unknown and complex mixtures are being analyzed, such as those encountered in air-oxidation reactions, and the rates of reaction of the component oxirane compounds with the hydrochloric acid-ether reagent are not known.

The authors have not experienced any difficulty in handling and storing the hydrochloric acid-ether solution. The solution is stored in glass-stoppered bottles, and the approximate constancy of the blanks, which are run with each set of analyses, indicates that there is little change in the composition of the reagent as a result of evaporation. Dioxane has been suggested as a solvent (1) for the anhydrous hydrochloric acid, but since ethyl ether has always been satisfactory, the authors have not investigated it.

Olefins which are not readily converted to chlorohydrins by reaction with hypochlorous acid give good yields of the chlorohydrins by reaction of the corresponding oxirane compounds (5, 7, 9, 10) with the hydrochloric acid-ether reagent described above.

Table IV. Analyses of Mixtures of 9,10-Epoxystearic Acid (Melting Point 59.5°) and *tert*-Butyl Hydroperoxide for Oxirane Oxygen

Mixture	Per Cent Oxirane Oxygen	
	Calcd.	Found
<i>tert</i> -Butyl hydroperoxide ^a , 100%	0.0	0.0
9,10-Epoxystearic acid, 0%		
<i>tert</i> -Butyl hydroperoxide ^a , 49.4%	2.71	2.70
9,10-Epoxystearic acid, 50.6%		
<i>tert</i> -Butyl hydroperoxide ^a , 23.4%	4.10	4.07
9,10-Epoxystearic acid, 76.6%		
<i>tert</i> -Butyl hydroperoxide, 0%	5.36	5.33
9,10-Epoxystearic acid, 100%		

^a 50% solution in *tert*-butyl alcohol.

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